



(72) Horn, Gerhardt, DE

(72) Frohning, Carl D., DE

(73) Hoechst Aktiengesellschaft, DE

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(54) **PROCEDE DE PREPARATION D'ALCOOLS**

(54) **PROCESS FOR THE PREPARATION OF ALCOHOLS (ONE-STAGE)**

(57) La présente invention a trait à un procédé pour la préparation d'alcools par réaction de composés organiques carbonylés ou de mélanges contenant des composés organiques carbonylés avec de l'hydrogène sur un catalyseur sur support contenant du nickel, de l'oxyde d'aluminium et du bioxyde de zirconium à température élevée et, au besoin, sous pression accrue. Les composés carbonylés qu'on fait réagir à des températures de 60 à 150°C sont des cétones, des aldéhydes et des dérivés de ces produits.

(57) The present invention relates to a process for the preparation of alcohols by reaction of organic carbonyl compounds or mixtures containing organic carbonyl compounds with hydrogen over a supported catalyst containing nickel, aluminum oxide and zirconium dioxide at elevated temperature and if appropriate under increased pressure. Ketones, aldehydes and derivatives thereof are reacted as the carbonyl compounds at temperatures of 60 to 150°C.

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Hoechst Aktiengesellschaft, 6230 Frankfurt am Main 80

Abstract of the disclosure:

Process for the preparation of alcohols (one-stage)

The present invention relates to a process for the preparation of alcohols by reaction of organic carbonyl compounds or mixtures containing organic carbonyl compounds with hydrogen over a supported catalyst containing nickel, aluminum oxide and zirconium dioxide at elevated temperature and if appropriate under increased pressure. Ketones, aldehydes and derivatives thereof are reacted as the carbonyl compounds at temperatures of 60 to 150°C.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of an alcohol by reaction of an organic carbonyl compound or a mixture containing a carbonyl compound with hydrogen in the presence of a hydrogenation catalyst at elevated temperature and if appropriate under increased pressure, which comprises reacting the carbonyl compound or the mixture at 60 to 150°C over a supported catalyst containing nickel, aluminum oxide and zirconium dioxide.
2. A process according to claim 1, wherein a ketone, derivative, aldehyde or aldehyde derivative is employed as the carbonyl compound.
3. A process according to claim 1, wherein an aldehyde or aldehyde derivative is employed as the carbonyl compound.
4. A process according to claim 3, wherein the aldehyde or aldehyde derivative is an aliphatic aldehyde or derivative.
5. A process according to any one of claims 1 to 4, wherein the hydrogenation catalyst contains 20 to 90% by weight of nickel, based on the catalyst composition, and 1 to 30 parts by weight of aluminum oxide and 0.5 to 20 parts by weight of zirconium dioxide, in each case per 100 parts by

weight of Ni, as a coprecipitate on a support material.

6. A process according to any one of claims 1 to 4, wherein the support material is active charcoal, alumina, pumice,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , silica gel, kieselguhr or silicic earth.

7. A process according to any one of claims 1 to 4, wherein the support material is  $\text{SiO}_2$ , silica gel, kieselguhr or silicic earth.

8. A process according to any one of claims 1 to 4, wherein the support material is kieselguhr or  $\text{SiO}_2$  in the form of precipitated silicic acid.

9. A process according to any one of claims 1 to 4, wherein the hydrogenation catalyst contains 6 to 80 parts by weight of support material per 100 parts by weight of Ni.

10. A process according to any one of claims 1 to 4, wherein the hydrogenation catalyst contains 15 to 65 parts by weight of support material per 100 parts by weight of Ni.

11. The process according to any one of claims 1 to 4, wherein the hydrogenation catalyst contains 35 to 50 parts by weight of support material per 100 parts by weight of Ni.

12. A process according to any one of claims 1 to 4,

wherein the reaction is carried out in the liquid phase at 60 to 150°C.

13. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the liquid phase at 80 to 140°C.

14. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the liquid phase at 90 to 130°C.

15. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the liquid phase at 100 to 125°C.

16. A process according to any one of claims 1 to 4, wherein the reaction is carried out at 0.1 to 25 MPa.

17. A process according to any one of claims 1 to 4, wherein the reaction is carried out at 1.0 to 15 MPa.

18. A process according to any one of claims 1 to 4, and 6, wherein the reaction is carried out at 2.0 to 10 MPa.

19. A process according to any one of claims 1 to 4 and 6, wherein the reaction is carried out in the liquid phase and the space velocity, expressed as the volume of liquid feed material/volume of catalyst x hour ( $V/V_h$ ) is 0.6 to 2.0.

20. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the liquid phase and the space velocity, expressed as the volume of liquid feed material/volume of catalyst x hour ( $V/V_h$ ) is 0.8 to 1.6.

21. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the liquid phase and the space velocity, expressed as the volume of liquid feed material/volume of catalyst x hour ( $V/V_h$ ) is 1.0 to 1.5.

22. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 60 to 150°C.

23. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 80 to 140°C.

24. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 90 to 130°C.

25. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 0.05 to 2.0 MPa.

26. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at

0.1 to 1.2 MPa.

27. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 0.15 to 1.0 MPa.

28. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gas phase and the volume of liquid feed material/volume of catalyst x hour (V/Vh) is 0.2 to 1.5.

29. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gas phase and the volume of liquid feed material/volume of catalyst x hour (V/Vh) is 0.3 to 1.2.

30. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gas phase and the volume of liquid feed material/volume of catalyst x hour (V/Vh) is 0.5 to 1.0.

31. A process according to any one of claims 1 to 4, wherein the reaction is carried out in the gaseous phase at 60 to 150°C under a pressure of 0.05 to 2.0 MPa.

FETHERSTONHAUGH & CO.  
OTTAWA, CANADA

PATENT AGENTS

Process for the preparation of alcohols (one-stage)

5 The present invention relates to a process for the  
preparation of alcohols starting from organic carbonyl  
compounds or mixtures containing organic carbonyl com-  
pounds. It is known that organic carbonyl compounds can  
be reacted with hydrogen in the presence of a hydrogenation  
catalyst at elevated temperature and if appropriate  
under increased pressure to give the corresponding  
alcohols. The reaction can be carried out either discontin-  
10 continuously or continuously in a homogeneous or heterogene-  
ous phase system. The hydrogenation catalyst is accord-  
ingly present either in dissolved form or in finely  
divided form as a suspension or in pieces as a fixed bed  
contact catalyst in the form of pieces. The carbonyl  
15 compounds to be hydrogenated can be passed to the  
catalyst in the gaseous or liquid state.

20 A comprehensive description of the preparation of alco-  
hols by catalytic hydrogenation of carbonyl compounds, in  
particular of ketones, aldehydes and derivatives thereof,  
can be found in Houben-Weyl, Methoden der organischen  
Chemie (Methods of Organic Chemistry), Georg Thieme  
Verlag Stuttgart-New York 1984, Volume VI/1b pages 9 to  
111.

25 DE-AS 12 70 018 describes a process for the preparation  
of alcohols by catalytic hydrogenation of aldehydes in  
the presence of a suspended catalyst, the gaseous hydro-  
gen being added to the reaction at a rate such that the  
catalyst is suspended in only part of the liquid phase.  
The liquid phase containing no catalyst is removed  
30 continuously. Raney nickel is used as a particularly  
suitable catalyst for carrying out this process.

35 DE-AS 12 31 227 relates to a process for the preparation  
of alcohols by continuous hydrogenation of aldehydes  
having 6 to 13 carbon atoms in the liquid phase using an  
amorphous nickel catalyst.



DE-OS 26 28 987 describes a process for the preparation of alcohols having 3 to 5 carbon atoms by reaction of the corresponding aldehydes in the liquid phase over a supported catalyst containing nickel, copper and manganese.

The processes described above for the preparation of alcohols leaves something to be desired in respect of the conversion and/or selectivity of the catalytic hydrogenation reaction. They furthermore require relatively long reaction times and high reaction temperatures.

There is therefore a need for an improved process compared with the prior art. The object is achieved by a process for the preparation of alcohols by reaction of organic carbonyl compounds or mixtures containing organic carbonyl compounds with hydrogen in the presence of a hydrogenation catalyst at elevated temperature and if appropriate under increased pressure.

The process comprises reacting the carbonyl compounds or the mixtures at 60 to 150°C over a supported catalyst containing nickel, aluminum oxide and zirconium dioxide.

Compared with processes according to the prior art, the process according to the invention in numerous cases enables the hydrogenation of carbonyl compounds to be carried out not only with an increased conversion but also with an increased selectivity. It furthermore renders it possible to allow the hydrogenation to proceed at lower temperatures and/or with shorter reaction times, i.e. with higher throughputs, in comparison with known procedures.

The process according to the invention can be used for the conversion of ketones, ketone derivatives, aldehydes and derivatives thereof.

Ketones which can be employed are acetone, methyl ethyl

ketone, diethyl ketone, hexanones, for example cyclohexanone, heptanones and octanones, and also higher ketones, as well as aromatic ketones, such as acetophenone and benzophenone, and ketone derivatives which can be employed are acetol (hydroxyacetone), acetoin (acetyl-methylcarbinol), dihydroxyacetone, benzoin and lactones, as well as ketoses, such as fructose.

Aromatic, araliphatic, cycloaliphatic and aliphatic aldehydes and derivatives thereof, in particular cycloaliphatic and aliphatic, preferably aliphatic, aldehydes and derivatives thereof, can be converted with the aid of the process according to the invention. The use of aliphatic straight-chain and branched aldehydes having 2 to 18 carbon atoms is of particular importance. With the exception of acetaldehyde, these aldehydes can be prepared, for example, by hydroformylation of olefins. They can be employed in the process according to the invention in prepurified form, and also as the crude product, for example as the crude hydroformylation product.

Suitable aldehydes are: acetaldehyde, propanal, n- and i-butanal, n- and i-pentanal, n- and i-hexanal, n- and i-heptanal, n- and i-octanal, n- and i-nonanal, n- and i-decanal and n- and i-alkanals having 11 to 18 carbon atoms, in particular acetaldehyde, propanal, n- and i-butanal, n- and i-pentanal, n- and i-octanal, n- and i-nonanal and alkanals having 11 to 18 carbon atoms, preferably propanal, n- and i-butanal, n- and i-octanal and n- and i-nonanal.

Unsaturated aldehydes can also be converted according to the invention. These include: acrolein, crotonaldehyde, n- and i-pentenal, n- and i-hexenal, n- and i-heptenal and n- and i-octenal, in particular acrolein, crotonaldehyde and 2-ethylhexenal, preferably 2-ethylhexenal.

Aldehyde derivatives are compounds which are derived from aldehydes. They can be prepared by a number of customary

syntheses, such as aldolization, aldol condensation and substitution or addition reactions - the addition of water onto unsaturated aldehydes may be mentioned - and can be converted according to the invention into the corresponding alcohols with good results.

Mixtures containing organic carbonyl compounds are solutions of the carbonyl compounds listed above, in particular dilute solutions thereof, and also crude reaction products such as are obtained, in particular in the dilute state, in the preparation of the carbonyl compounds, for example by aldolization, aldol condensation, hydroformylation, substitution or addition.

Although such mixtures often contain the carbonyl compounds in a reduced and sometimes even only quite low concentration, they can be converted according to the invention into the corresponding alcohols with good results.

The hydrogenation catalyst contains 20 to 90% by weight of nickel, based on the catalyst composition, and 1 to 30, in particular 3 to 15, preferably 4 to 10 parts by weight of aluminum oxide and 0.5 to 20, in particular 1 to 10, preferably 1.5 to 5 parts by weight of zirconium dioxide, in each case per 100 parts by weight of nickel, as a coprecipitate on a support material.

Since the carrying out of the process according to the invention is linked to this particular catalyst, its preparation will be illustrated in more detail below.

An aqueous Ni-Al-Zr mixed salt solution is mixed with an aqueous solution of a basic compound as a precipitating agent, the basic compound being employed in a stoichiometric excess of 5 to 100%, based on the amount required for quantitative precipitation of Ni, Al and Zr, and Ni, Al and Zr are precipitated simultaneously at 60 to 120°C and pH 7 to 10 and deposited as a coprecipitate on a

support material.

5 In order to prevent undesirable hydrolysis and to provide a favorable influence on the precipitation, it is advisable for free acid to be added to the mixed salt solution in an excess corresponding to a ratio of  $H^+ : Zr^{4+} = (2 \text{ to } 40) : 1$ , in particular  $(3 \text{ to } 30) : 1$ , preferably  $(4 \text{ to } 20) : 1$ . The free acid is determined by titration with NaOH (end point pH = 0.8).

10 Hydrochloric acid, sulfuric acid and preferably nitric acid can be employed as the free acid.

15 The mixed salt solution consists of 10 to 100, in particular 20 to 80, preferably 30 to 50 g of Ni/l. It contains aluminum corresponding to 1 to 30, in particular 3 to 15, preferably 4 to 10 parts by weight of  $Al_2O_3$  per 100 parts by weight of Ni. It furthermore contains zirconium corresponding to 0.5 to 20, in particular 1 to 10, preferably 1.5 to 5 parts by weight of  $ZrO_2$  per 100 parts by weight of Ni.

20 The mixed salt solution is prepared by dissolving water-soluble inorganic, organic or complex salts of nickel, zirconium and aluminum, in particular sulfates, chlorides, acetates and nitrates thereof, preferably nitrates thereof, in water.

25 An aqueous solution of a basic compound, in particular an aqueous alkali metal carbonate, alkali metal bicarbonate, alkali metal hydroxide, ammonium hydroxide or ammonium carbonate solution, which has a pH of 7.5 to 13, in particular 8 to 12, preferably 9 to 11, is used as the precipitating agent.

30 Aqueous solutions containing 0.3 to 1.5, in particular 0.8 to 1.2 mol of alkali metal carbonate/l of solution produce quite good results.

In order to ensure as complete as possible a precipitation of a particularly homogeneous coprecipitate, the basic compound is employed in a stoichiometric excess of 5 to 100, in particular 10 to 70, preferably 20 to 40%,  
5 in each case based on the amount of basic compound required for complete precipitation of Ni, Al and Zr.

The precipitation is brought about either by bringing together and mixing the mixed salt solution and the precipitating agent continuously or, according to a  
10 preferred variant, by initially introducing the precipitating agent into the vessel and introducing the mixed salt solution into the precipitating agent.

The support material can be employed in the reaction with the mixed salt solution and/or with the precipitating  
15 agent.

It has proved to be particularly advantageous first to mix the mixed salt solution and the precipitating agent with one another and then to add the support material.

Suitable support materials are active charcoal, aluminas, pumice,  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , silica gel, kieselguhr and silicic  
20 earths.  $\text{SiO}_2$ , silica gel, kieselguhr and silicic earth have proved to be particularly suitable. Kieselguhr and  $\text{SiO}_2$  in the form of precipitated silicic acid are preferably employed.

6 to 80, in particular 15 to 65, preferably 35 to 50 parts by weight of support material are usually  
25 employed per 100 parts by weight of Ni.

To prepare homogeneous coprecipitates, a pH range of 7 to 10, in particular 7.3 to 9, preferably 7.5 to 8.5, and a  
30 temperature of 60 to 120, in particular 70 to 110, preferably 95 to 105°C are maintained during the precipitation.

When the precipitation has ended, and if appropriate after cooling, the mixture is filtered and the product is washed, shaped if required and then dried and reduced.

5     Drying is carried out in a temperature range between 40 and 120, in particular 50 and 100°C.

10     The reduction by means of hydrogen is carried out at 300 to 550°C, a degree of reduction of at least 80%, in particular at least 90%, preferably 95% or more, being aimed for. The degree of reduction is understood as the content of nickel metal: total nickel content x 100%. ] -

15     The process according to the invention for the preparation of alcohols by reaction of organic carbonyl compounds with hydrogen in the presence of the catalyst described above can be carried out discontinuously or continuously.

20     If the process is carried out in the liquid phase, the catalyst can be employed either as a finely divided suspension or in the form of pieces as a fixed bed contact catalyst. The reaction temperature is 60 to 150°C. If particularly gentle conditions are required, a reaction temperature of 60 to 80°C is used. In most cases, the hydrogenation according to the invention can be carried out at temperatures of 80 to 140°C, in particular 90 to 130°C, preferably 100 to 125°C. The pressure is usually 0.1 to 25, in particular 1.0 to 15, preferably 2.0 to 10 MPa.

30     The carbonyl compound to be reacted is either passed in liquid form, together with hydrogen, batchwise or continuously to the suspended catalyst, or the feed material containing the carbonyl compound is passed in co- or countercurrent with hydrogen over the supported catalyst containing nickel, aluminum oxide and zirconium oxide, which is in the form of pieces and arranged as a fixed bed. When carrying out the process according to the

invention industrially, the fixed bed procedure will probably often be preferred, the feed mixture being passed over the catalyst arranged as a fixed bed either from the top downwards (trickle procedure) or from the bottom upwards (sump procedure). If the trickle procedure is used, the hydrogen is passed in co- or countercurrent, preferably in co-current, with the feed material, whereas if the sump procedure is to be practised, the hydrogen is advantageously passed in co-current with the feed mixture over the supported catalyst in the form of pieces arranged in a fixed bed.

If the process is carried out continuously in the liquid phase, the space velocity, expressed as the volume of liquid feed material/volume of catalyst x hour ( $V/V_h$ ), is 0.6 to 2.0, in particular 0.8 to 1.6, preferably 1.0 to 1.5.

Hydrogen at least corresponding to the stoichiometry of the reaction must be employed. As a rule, however, a stoichiometric excess of hydrogen will be used in order to have a favorable influence on the reaction. An excess of hydrogen of 1 to 100, in particular 2 to 50, preferably 5 to 10 mol per equivalent of carbonyl compounds is sufficient for carrying out the hydrogenation in the liquid phase. Unreacted hydrogen can be recycled into the reaction.

However, the process according to the invention is also suitable for carrying out in the gas phase, the feed material being passed in the gaseous state, together with hydrogen, over the supported catalyst containing nickel, aluminum and zirconium dioxide, which is in the form of pieces arranged in a fixed bed.

The reaction in the gas phase is carried out at 60 to 150°C. In most cases, a temperature of 80 to 140, in particular 90 to 130°C is sufficient. The pressure is 0.05 to 2.0, in particular 0.1 to 1.2, preferably 0.15 to

1.0 MPa.

If the process is carried out continuously in the gas phase, the space velocity, expressed as the volume of liquid feed material/volume of catalyst x hour (V/Vh), is 5 0.2 to 1.5, in particular 0.3 to 1.2, preferably 0.5 to 1.0.

Hydrogen corresponding to at least the stoichiometry of the reaction must be employed. However, a stoichiometric excess of hydrogen is usually used in order to guide the 10 reaction in the desired direction. An excess of hydrogen of 0.5 to 50, in particular 1 to 20, preferably 2 to 10 mol per equivalent of carbonyl compound proves to be adequate for the gas phase hydrogenation. Unreacted hydrogen can be recycled into the reaction.

15 The procedure used depends on the one hand on the nature of the carbonyl compound and on the other hand on the apparatuses available in which the reaction is to be carried out. No general recommendation giving one of the process variants illustrated above preference can be 20 stated in view of the wide use possibilities of the process according to the invention.

The examples listed below demonstrate the present invention without limiting it.

#### Experimental part

##### 25 Example 1

400 g of n-butanal and 2.4 g of a catalyst which contains 100 parts by weight of Ni, 5 parts by weight of aluminum oxide and 3 parts by weight of zirconium dioxide as a coprecipitate and 40 parts by weight of SiO<sub>2</sub> as the 30 support are initially introduced into an autoclave (volume 1000 ml) provided with a magnetic piston stirrer, with exclusion of air. Hydrogen is then forced in, the mixture is heated up, while stirring, and the desired



### Reaction conditions

10 Comparison Example 1

### Reaction conditions

### Example 2

30 The procedure is then as described in Example 1.

## Reaction conditions

Pressure 8.0 MPa  
Temperature 120°C  
Hydrogenation time 60 minutes

- 5 The hydrogenation product has a CO number of only 0.5 (mg of KOH/g), corresponding to 0.1% by weight of octanal, and an iodine number of 2.5 (g of I<sub>2</sub>/100 g).

Comparison Example 2

- 10 The procedure is as in Example 2, except that a customary catalyst containing about 65% by weight of Ni,

but which contains no nickel-aluminum oxide-zirconium dioxide coprecipitate, is used.

## Reaction conditions

- 15 Pressure 8.0 MPa  
Temperature 120°C  
Hydrogenation time 75 minutes

- 20 The hydrogenation product has a CO number of 3.2 (mg of KOH/g), corresponding to 0.8% by weight of octanal, and an iodine number of 12.5 (g of I<sub>2</sub>/100 g).

Example 3

- 25 400 g of a mixture which, corresponding to a CO number of 234 (mg of KOH/g), contains about 59% by weight of i-nonanal (prepared by hydroformylation of diisobutylene) and unsaturated compounds corresponding to an iodine number of 36 (g of I<sub>2</sub>/100 g) and 7.5 g of the catalyst used in Example 1 are initially introduced into an autoclave (volume 1000 ml) provided with a magnetic piston stirrer. The procedure is then as described in
- 30 Example 1.

## Reaction conditions

Pressure 8.0 MPa  
Temperature 120°C

Hydrogenation time 60 to 70 minutes

5 The hydrogenation product has a CO number of only 0.2 to 0.3 (mg of KOH/g), corresponding to about 0.1% by weight of i-nonanal, and an iodine number of only 0.2 to 0.3 (g of I<sub>2</sub>/100 g).

Comparison Example 3

The procedure is as in Example 3, except that the catalyst used in Comparison Example 1 is employed.

Reaction conditions

10           Pressure               8.0 MPa  
            Temperature           120°C  
            Hydrogenation time   85 minutes

15 The hydrogenation product has a CO number of 0.5 to 0.6 (mg of KOH/g), corresponding to 0.2 to 0.3% by weight of i-nonanal, and an iodine number of 12 (g of I<sub>2</sub>/100 g).

Example 4

20 400 g of a mixture which, in addition to 1.2% by weight of n-propanol, 8.1% by weight of by-products and about 83% by weight of (i-butanol + water), also contains about 7.5% by weight of β-hydroxypropanal (demonstrated by gas chromatographic analysis) and 6.7 g of the catalyst used in Example 1 are initially introduced into an autoclave (volume 1000 ml) provided with a magnetic piston stirrer. The procedure is then as described in Example 1.

25           Reaction conditions

            Pressure               8.0 MPa  
            Temperature           90°C  
            Hydrogenation time   40 minutes

30 The hydrogenation product has a CO number of 0.78 (mg of KOH/g), corresponding to <0.1% by weight of β-hydroxypropanal. According to analysis by gas chromatography, it has the following composition:

	First runnings	0.1 % by weight
	n-Propanol	1.3 % by weight
	By-products	7.3 % by weight
	$\beta$ -Hydroxypropanal	<0.1 % by weight
5	Propane-1,3-diol	7.7 % by weight
	i-Butanol + water	83.5 % by weight

#### Comparison Example 4

The procedure is as in Example 4, except that the catalyst used in Comparison Example 1 is employed.

10	Reaction conditions	
	Pressure	8.0 MPa
	Temperature	90°C
	Hydrogenation time	210 minutes

15 According to analysis by gas chromatography, the hydrogenation product has the following composition:

	First runnings	0.1 % by weight
	n-Propanol	1.4 % by weight
	By-products	9.4 % by weight
	$\beta$ -Hydroxypropanal	<0.1 % by weight
20	Propane-1,3-diol	7.3 % by weight
	i-Butanol + water	81.8 % by weight

25 As a comparison of Example 4 and Comparison Example 4 shows, according to the invention the reaction of the  $\beta$ -hydroxypropanal takes place in a considerably shorter time with at the same time less formation of by-products.

#### Example 5

30 400 g of a mixture which, corresponding to a CO number of 12.7 (mg of KOH/g), contains predominantly n-butanol, and 1.6% by weight of n-butanal and unsaturated compounds corresponding to an iodine number of 2 to 4 (g of I<sub>2</sub>/100g)

and 25 g of the catalyst used in Example 1 are initially introduced into an autoclave (volume 1000 ml) provided with a magnetic piston stirrer. The procedure is then as described in Example 1.

5      Reaction conditions

Pressure                      8.0 MPa  
Temperature                  115°C  
Hydrogenation time      120 minutes

10      The hydrogenation product has a CO number of 0.04 (mg of KOH/g), corresponding to 0.005% by weight of n-butanal, and an iodine number of 0.01 (g of I<sub>2</sub>/100 g).

Comparison Example 5

The procedure is as in Example 5, except that the catalyst used in Comparison Example 1 is employed.

15      Reaction conditions

Pressure                      8.0 MPa  
Temperature                  115°C  
Hydrogenation time      120 minutes

20      The hydrogenation product has a CO number of 1.95 (mg of KOH/g), corresponding to 0.25% by weight of n-butanal, and an iodine number of 0.17 (g of I<sub>2</sub>/100 g).

Example 6 (continuous hydrogenation in the liquid phase)

25      A vertical tube contains 1000 ml of bulk catalyst (pelleted form) used in Example 1. 1000 ml per hour of a liquid mixture which contains predominantly n-butanol and, corresponding to a CO number of 10 to 13 (mg of KOH/g), 1.3 to 1.8% by weight of n-butanal and unsaturated compounds corresponding to an iodine number of 1.5 to 2.4 (g of I<sub>2</sub>/100 g) are passed over the bulk catalyst from the bottom upwards in co-current with hydrogen.

30

## Reaction conditions

Pressure	8.0 MPa
Temperature	105°C
Hydrogen	100 l (s.t.p.)/hour

- 5 The hydrogenation product has a CO number of 0.1 to 0.5, corresponding to 0.012 to 0.06% by weight of n-butanal, and an iodine number of 0.01 (g of I<sub>2</sub>/100 g).

Comparison Example 6 (continuous hydrogenation in the liquid phase)

- 10 The procedure is as in Example 6, the vertical tube containing 1000 ml of bulk catalyst (pelleted form) used in Comparison Example 1. The same feed mixture as in Example 6 is passed over the bulk catalyst, but only in an amount of 250 to 300 ml per hour.

15 Reaction conditions

Pressure	8.0 MPa
Temperature	120°C
Hydrogen	25 to 30 l (s.t.p.)/hour

- 20 The hydrogenation product has a CO number of 0.6 to 1.6 (mg of KOH/g), corresponding to 0.08 to 0.2% by weight of n-butanal.

- 25 As the direct comparison in Example 6 shows, the process according to the invention allows a throughput which is 3 to 4 times higher and at the same time a better conversion (demonstrated by the CO number) and lower reaction temperature.

Example 7 (continuous hydrogenation in the liquid phase)

- 30 A vertical tube contains 1000 ml of bulk catalyst (pelleted form) used in Example 1. 1100 ml per hour of a liquid mixture which contains predominantly 2-ethylhexanol and, corresponding to a CO number of 4.9 (mg of KOH/g), 1.1% by weight of (2-ethylhexanal + 2-ethylhexenal) and unsaturated compounds (2-ethylhexenal +

other unsaturated compounds) corresponding to an iodine number of 1.6 (g of  $I_2$ /100 g) are passed over the bulk catalyst from the top downwards in co-current with hydrogen.

5      Reaction conditions

Pressure	2.5 MPa
Temperature	115°C
Hydrogen	120 l (s.t.p.)/hour

10      The hydrogenation product has a CO number of 0.041 (mg of KOH/g), corresponding to 0.009% by weight of (2-ethylhexanal + 2-ethylhexenal) and an iodine number of 0.028 (g of  $I_2$ /100 g).

Comparison Example 7 (continuous hydrogenation in the liquid phase)

15      The procedure is as in Example 7, the vertical tube containing 1000 ml of bulk catalyst (pelleted form) used in Comparison Example 1. 700 ml per hour of a liquid mixture which contains predominantly 2-ethylhexanol and, corresponding to a CO number of 3.0 to 3.7 (mg of KOH/g),  
20      0.68 to 0.84% by weight of (2-ethylhexanal + 2-ethylhexenal) and unsaturated compounds (2-ethylhexenal + other unsaturated compounds) corresponding to an iodine number of 1.6 (g of  $I_2$ /100 g) are passed over the bulk catalyst from the top downwards in co-current with  
25      hydrogen.

Reaction conditions

Pressure	2.5 MPa
Temperature	130°C
Hydrogen	76 l (s.t.p.)/hour

30      As the direct comparison in Example 7 shows, the process according to the invention allows a significantly higher throughput (that is to say V/Vh of 1.1, instead of V/Vh of 0.7) and in spite of a lower reaction temperature leads to a product of improved quality (demonstrated by

the CO number and iodine number).

Example 8 (continuous hydrogenation in the gas phase)

5 A vertical tube contains 1000 ml of bulk catalyst  
(pelleted form) used in Example 1. 500 ml per hour of a  
mixture which contains 65 to 75% by weight of n- and i-  
butanal, 8 to 15% by weight of n- and i-butanol, 3.5 to  
5.5% by weight of n- and i-butyl formate and 1 to 3% by  
weight of n- and i-dibutyl ether (demonstrated by analy-  
sis by gas chromatography) are fed to a vaporizer. The  
10 mixture is passed in the gaseous state over the bulk  
catalyst from the top downwards in co-current with  
hydrogen.

Reaction conditions

15	Pressure:	0.2 MPa
	Temperature:	90°C
	V/Vh*:	0.5
	Hydrogen:	2200 l (s.t.p.)/hour

20 According to analysis by gas chromatography, the hydroge-  
nation product contains 0.2 to 0.4% by weight of n- and  
i-butanal, 96.3 to 98.1% by weight of n- and i-butanol,  
1.2 to 1.8% by weight of n- and i-butyl formate and 0.5  
to 1.5% by weight of n- and i-dibutyl ether.

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\* Space velocity (volume of liquid feed material/volume  
of catalyst x hour)